

THE SMALL VIBRATIONS OF CERTAIN MECHANICAL SYSTEMS

- A. The Elastic Character of the Homopolar Chemical Bond.
- B. Study of the Small Vibrations of Six Particles in a System Analogous to the Benzene Ring.

BY
ROBERT C. YATES

A DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN PARTIAL
FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY
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THE ELASTIC CHARACTER OF THE HOMOPOLAR
CHEMICAL BOND

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(Received June 23, 1930)

ABSTRACT

An attempt is made to obtain frequencies of internal vibrations of some organic molecules by the consideration of certain mechanical systems.

The system of three particles is studied assuming the forces of restitution elastic. Certain proportionality constants are determined, using a representative compound, which characterize the single valence bond. Calculated wave-numbers for CO_2 , CS_2 , CH_2Cl_2 , $\text{C}_2\text{H}_5\text{OH}$ are compared with observed data from Raman spectra.

I. INTRODUCTION

THERE has been a recent impulse on the part of the physical chemist to determine precisely the character of the chemical bond that retains the atoms in mutual attraction in molecular structures of organic compounds. An attempt in this direction has been made¹ under the assumption that the valence bond is of spring-like nature and the forces set up by a displacement are elastic. Mechanical models of representative molecules have been constructed accordingly and experiments run to observe the fundamental modes of vibration.² The correlation between such observed frequencies and those obtained from the Raman spectra was found to be surprisingly good. This prompted the desire to look more closely into several types of systems and to set up the dynamical equations of motion yielding frequencies that might be compared with experiment.

II. STATEMENT OF THE PROBLEM

We shall thus be concerned with the small vibrations of a system of particles about a position of stable equilibrium under certain definite assumptions, these assumptions to be supported by the closeness of agreement in the end.

The intramolecular forces that arise are set up by the mutual attraction and repulsion of the atoms, suggesting not only an elastic force between any two but also a force of restoration dependent on the angular divergence of neighboring bonds.

Definitely, it is assumed that the force tending to restore a particle after a displacement is the sum of two types of forces: the first acting along the

¹ D. H. Andrews, *The Relation Between the Raman Spectra and the Molecular Structure of Organic Compounds*, p. 544, this issue.

² F. Kettering, L. W. Shutts, D. H. Andrews, *A Representation of the Dynamic Properties of Molecules by Mechanical Models*, p. 531, this issue.

line of connection with another particle and proportional to the linear displacement (Hooke's law); the second acting at right angles to the first and proportional to the change in the angle between two adjoining bonds. This last may be restated as being proportional to the arc displacement.

We consider here only small displacements and higher order infinitesimals, in the presence of those of lower order, are neglected throughout. The motion of the particles is assumed to be in a given plane.

III. DETERMINATION OF THE FORCE CONSTANT k_1

Consider two particles of masses m_1 and m_2 constrained to linear motion. Assuming the force acting between them proportional to the displacement we find as is well known the frequency of vibration given by

$$\nu = (1/2\pi)(k_1/M)^{1/2} \quad (1)$$

where M denotes the relative mass $1/m_1 + 1/m_2$ and k_1 a factor of proportionality. If $m_1 = m_2 \equiv m$, we have

$$k_1 = 2\pi^2\nu^2m. \quad (2)$$

In order to evaluate k_1 we take the carbon-carbon combination of the diatomic molecule and assign the wave number of 1000 to motion along the line of connection.¹ This gives approximately $k_1 = 4 \times 10^5$ dynes per cm.

Before we may find a corresponding value for the remaining constant k_2 , that controls the restoring force arising from a change in the angle between neighboring bonds, we must look first at the system of three particles.

IV. THE SYSTEM OF THREE PARTICLES

Consider the system of three particles of masses m_1, m_2, m_3 , connected by two bonds as shown. We place the particles at the vertices of an isosceles triangle and select a reference frame with horizontal axis parallel to its base. These give the relations

$$\left. \begin{aligned} 2f/m_3 &= b/m_1 - c/m_2 \\ m_1d &= m_2a \end{aligned} \right\} \quad (3)$$

If the origin of coordinates be taken at the center of mass, we have

$$\left. \begin{aligned} f &= c - b \\ g &= a + d \end{aligned} \right\} \quad (4)$$

We introduce the notation:

$$\left. \begin{aligned} A &\equiv g/m_3 + a/m_1 \\ B &\equiv c/m_2 + f/m_3 = b/m_1 - f/m_3 \end{aligned} \right\} \quad (5)$$

so that $\tan \theta_2 = A/B$

Let the system be displaced to a position shown and let the components of displacement of the particles be $(1/m_i) \cdot (x_i, y_i)$.

The kinetic energy of the system is:

$$T = (\frac{1}{2})[(\dot{x}_1^2 + \dot{y}_1^2)/m_1 + (\dot{x}_2^2 + \dot{y}_2^2)/m_2 + (\dot{x}_3^2 + \dot{y}_3^2)/m_3]. \quad (6)$$

The potential energy—dependent on the configuration—is composed of a potential V_1 due to linear displacement and V_2 due to rotation:

$$V_1 = (k_1/2)(\Delta d_1^2 + \Delta d_2^2) \quad (7)$$

$$V_2 = (k_2/2) \cdot \Delta S^2 = (k_2 d_1^2/2) \cdot \Delta \phi^2.$$

In order to find the explicit expressions for the quantities in (7) we obtain from the figure:

$$\left. \begin{aligned} d_1 \cdot \Delta d_1 &= -A(y_1/m_1 - y_3/m_3) + B(x_1/m_1 - x_3/m_3) \text{ etc.} \\ d_1^2 \cdot \Delta \phi &= d_1^2(\Delta \theta_1 - \Delta \theta_2) = A(x_1/m_1 - x_2/m_2) + B(y_1/m_1 + y_2/m_2 - 2y_3/m_3) \end{aligned} \right\} (8)$$

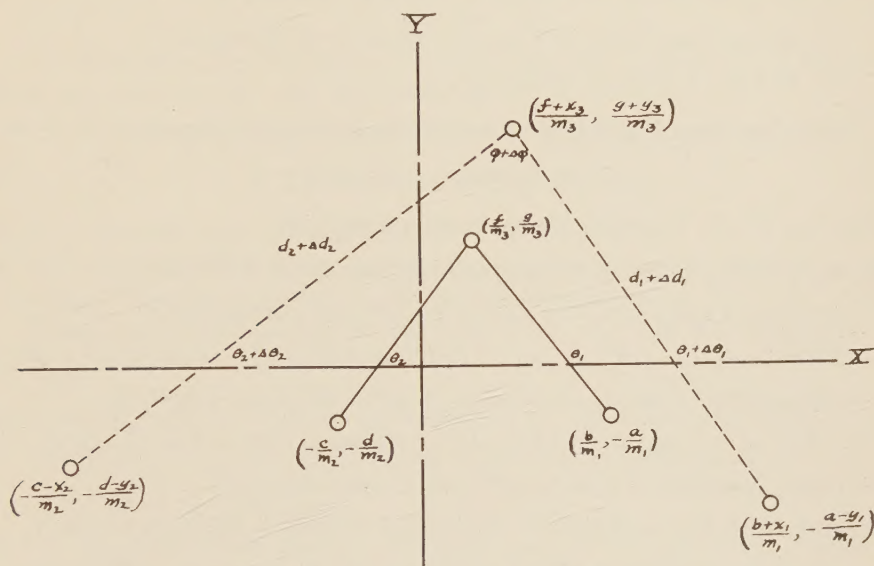


Fig. 1. System of three particles.

Since the resultant of the forces on the system is zero the center of mass will remain at rest in an inertial system. We may, therefore, write

$$\left. \begin{aligned} x_1 + x_2 + x_3 &= 0 \\ y_1 + y_2 + y_3 &= 0 \end{aligned} \right\} \quad (9)$$

Furthermore the moment of the various forces about the origin is zero so that the angular momentum of the system about the origin is constant. Assuming that this angular momentum is zero, we have:

$$\begin{aligned} m_1 \left| \begin{array}{cc} (b+x_1)/m_1 & -(a-y_1)/m_1 \\ \dot{x}_1/m_1 & \dot{y}_1/m_1 \end{array} \right| + m_2 \left| \begin{array}{cc} (c-x_2)/m_2 & -(d-y_2)/m_2 \\ \dot{x}_2/m_2 & \dot{y}_2/m_2 \end{array} \right| \\ + m_3 \left| \begin{array}{cc} (f+x_3)/m_3 & (g+y_3)/m_3 \\ \dot{x}_3/m_3 & \dot{y}_3/m_3 \end{array} \right| = 0 \end{aligned} \quad (10)$$

which becomes on integrating:

$$By_2 = A(x_1 + x_2) + By_1. \quad (11)$$

The two energy functions may now be rewritten, because of the relations Eq. (9) and Eq. (11):

$$T = (\frac{1}{2}B^2) \{ [B^2/m_1 + A^2/m_2 + (A^2 + B^2)/m_3] \dot{x}_1^2 + (A^2 + B^2)(1/m_2 + 1/m_3) \dot{x}_2^2 + B^2(1/m_1 + 1/m_2 + 4/m_3) \dot{y}_1^2 + 2[A^2/m_2 + (A^2 + B^2)/m_3] \dot{x}_1 \dot{x}_2 + 2AB(1/m_2 + 2/m_3)(\dot{x}_1 + \dot{x}_2) \dot{y}_1 \} \quad (12)$$

$$V = (k_1/2d_1^2) \{ [(A^2 - B^2)/m_3 - B^2/m_1] x_1 + [(A^2 - B^2)/m_3] x_2 + AB(2/m_3 + 1/m_1) y_1 \}^2 + (k_1/2d_1^2) \{ [(A^2 + B^2)/m_3 + A^2/m_2] x_1 + (A^2 + B^2)(1/m_2 + 1/m_3) x_2 + AB(2/m_3 + 1/m_2) y_1 \}^2 + (k_2/2d_1^2) \{ AB(1/m_1 + 1/m_2 + 2/m_3) x_1 + (2AB/m_3) x_2 + B^2(1/m_1 + 1/m_2 + 4/m_3) y_1 \}^2. \quad (13)^*$$

These functions T and V must satisfy the Lagrangian equations of motion:

$$(d/dt)(\partial L/\partial \dot{x}_i) - (\partial L/\partial x_i) = 0 \quad (14)$$

where $L = T - V$. Inserting the expression L we have:

$$\begin{aligned} & [B^2/m_1 + A^2/m_2 + (A^2 + B^2)/m_3] \ddot{x}_1 + [A^2/m_2 + (A^2 + B^2)/m_3] \ddot{x}_2 + AB[2/m_3 + 1/m_2] \ddot{y}_1 = - (k_1/d_1^2) [(A^2 - B^2)/m_3 - B^2/m_1] \{ [(A^2 - B^2)/m_3 - B^2/m_1] x_1 + [(A^2 - B^2)/m_3] x_2 + AB[2/m_3 + 1/m_2] y_1 \} - (k_1/d_1^2) [(A^2 + B^2)/m_3 + A^2/m_2] \{ [(A^2 + B^2)/m_3 + A^2/m_2] x_1 + [A^2 + B^2][1/m_3 + 1/m_2] x_2 + AB[2/m_3 + 1/m_2] y_1 \} - (B^2 k_2/d_1^2) \cdot A \cdot [1/m_1 + 1/m_2 + 2/m_3] \{ A[1/m_1 + 1/m_2 + 2/m_3] x_1 + [2A/m_3] x_2 + B[1/m_1 + 1/m_2 + 4/m_3] y_1 \} \\ & [A^2/m_2 + (A^2 + B^2)/m_3] \ddot{x}_1 + (A^2 + B^2)[1/m_1 + 1/m_3] \ddot{x}_2 + AB[2/m_3 + 1/m_2] \ddot{y}_1 = - (k_1/d_1^2) [(A^2 - B^2)/m_3] \{ [(A^2 - B^2)/m_3 - B^2/m_1] x_1 + [(A^2 - B^2)/m_3] x_2 + AB[2/m_3 + 1/m_1] y_1 \} - (k_1/d_1^2) [A^2 + B^2][1/m_2 + 1/m_3] \{ [(A^2 + B^2)/m_3 + A^2/m_2] x_1 + (A^2 + B^2)[1/m_2 + 1/m_3] x_2 + AB[2/m_3 + 1/m_2] y_1 \} - (B^2 k_2/d_1^2) (2A/m_3) \{ A[1/m_1 + 1/m_2 + 2/m_3] x_1 + [2A/m_3] x_2 + B[1/m_1 + 1/m_2 + 4/m_3] y_1 \} \end{aligned} \quad (15)$$

$$\begin{aligned} & A[1/m_2 + 2/m_3] [\ddot{x}_1 + \ddot{x}_2] + B[1/m_1 + 1/m_2 + 4/m_3] \ddot{y}_1 = - (Ak_1/d_1^2) (2/m_3 + 1/m_1) \{ [(A^2 - B^2)/m_3 - B^2/m_1] x_1 + [(A^2 - B^2)/m_3] x_2 + AB[2/m_3 + 1/m_1] y_1 \} - (Ak_1/d_1^2) (2/m_3 + 1/m_2) \{ [(A^2 + B^2)/m_3 + A^2/m_2] x_1 + [A^2 + B^2][1/m_2 + 1/m_3] x_2 + AB[2/m_3 + 1/m_2] y_1 \} - (B^2 k_2/d_1^2) (1/m_1 + 1/m_2 + 4/m_3) \{ A[1/m_1 + 1/m_2 + 2/m_3] x_1 + [2A/m_3] x_2 + B[1/m_1 + 1/m_2 + 4/m_3] y_1 \}. \end{aligned} \quad (16)$$

These three Eqs. (15, 16, 17) define the motion of the system and are sufficient to determine the independent quantities x_1 , x_2 , y_1 .

* That the potential function as here written gives the correct forces is seen by calculating straight forwardly the forces acting on the separate particles. For example, the horizontal component of force acting on the first particle is $-(\delta V/\delta \cdot x_1/m_1)$.

On combining these we find:

$$\begin{aligned}
 & [B^2/m_1 + A^2/m_2 + 2B^2/m_3]\ddot{x}_1 + [(A^2 + B^2)/m_2 + 2B^2/m_3]\ddot{x}_2 + AB[1/m_2 - 1/m_1]\ddot{y}_1 \\
 & = (k_1/d_1^2) \{ [(A^2 + B^2)/m_1 + 2B^2/m_3] \{ [(A^2 - B^2)/m_3 - B^2/m_1]x_1 \\
 & + [(A^2 - B^2)/m_3]x_2 + AB[2/m_3 + 1/m_1]y_1 \} - (k_1/d_1^2) [(A^2 + B^2)/m_2 \\
 & + 2B^2/m_3] \{ [A^2/m_2 + (A^2 + B^2)/m_3]x_1 + [A^2 + B^2][1/m_2 + 1/m_3]x_2 \\
 & + AB[2/m_3 + 1/m_2]y_1 \}
 \end{aligned} \quad (18)$$

which defines the particular type of motion that is unaffected by any bending of the bonds.

IV (B)

We now make the restriction that the two end particles be of the same mass, say $m_1 = m_2 \equiv m$. Eq. (18) becomes:

$$\begin{aligned}
 \ddot{x}_1 + \ddot{x}_2 & = - (k_1/d_1^2) [(A^2 + B^2)/m + 2B^2/m_3](x_1 + x_2) \\
 & = - k_1(1/m + 2 \cos^2 \theta/m_3)(x_1 + x_2)
 \end{aligned} \quad (19)$$

where θ is a base angle (see table).

Thus the combined horizontal motion of the two end particles is simply harmonic. The third particle oscillates complementary to this.

Under this first restriction we solve Eqs. (15, 16, 17) explicitly for $\ddot{x}_1$, $\ddot{x}_2$, $\ddot{y}_1$:

$$\begin{aligned}
 \ddot{x}_1 & = (k_1/d_1^2) \{ [(A^2 - B^2)/m_3 - B^2/m]x_1 + [(A^2 - B^2)/m_3]x_2 + AB[2/m_3 \\
 & + 1/m]y_1 \} - (2Ak_2/d_1^2) \{ A[1/m + 1/m_3]x_1 + [A/m_3]x_2 \\
 & + B[2/m_3 + 1/m]y_1 \} \\
 \ddot{x}_2 & = - (k_1/d_1^2) \{ [A^2/m + (A^2 + B^2)/m_3]x_1 + [A^2 + B^2][1/m + 1/m_3]x_2 \\
 & + AB[2/m_3 + 1/m]y_1 \} + (2Ak_2/d_1^2) \{ A[1/m + 1/m_3]x_1 + [A/m_3]x_2 \\
 & + B[2/m_3 + 1/m]y_1 \} \\
 \ddot{y}_1 & = - (Ak_1/d_1^2B) \{ [(A^2 - B^2)/m_3 - B^2/m]x_1 + [(A^2 - B^2)/m_3]x_2 \\
 & + AB[2/m_3 + 1/m]y_1 \} - (2Bk_2/d_1^2) \{ A[1/m + 1/m_3]x_1 + [A/m_3]x_2 \\
 & + B[2/m_3 + 1/m]y_1 \}.
 \end{aligned} \quad (20)$$

If we are to find solutions of the type $x_i = C_i e^{\alpha t}$ for the differential equations (Eq. 20) we must require the vanishing of the determinant of coefficients:

$$\begin{vmatrix} \alpha^2 + a_{11} & a_{21} & a_{31} \\ a_{12} & \alpha^2 + a_{22} & a_{32} \\ a_{13} & a_{23} & \alpha^2 + a_{33} \end{vmatrix} = 0 \quad (21)$$

which is the characteristic equation—a cubic in α^2 —where the quantities a_{ij} are the constant coefficients that occur in the differential Eq. (20).

The determinant is readily reduced to:

$$\begin{vmatrix} \alpha^2 + b_{11} & 0 & 0 \\ a_{12} & \alpha^2 + b_{22} & a_{32} \\ a_{13} & b_{23} & \alpha^2 + a_{33} \end{vmatrix} = 0 \quad (22)$$

where

$$b_{11} = (k_1/d_1^2) [(A^2 + B^2)/m + 2B^2/m_3]$$

$$b_{22} = k_1 B^2/d_1^2 \cdot m + 2A^2 k_2/d_1^2 m$$

$$b_{23} = ABk_1/d_1^2 m - 2ABk_2/d_1^2 m$$

Solving Eq. (22) we get the two factors:

$$\alpha^2 + k_1(1/m + 2 \cos^2 \theta/m_3) = 0 \quad (23)$$

$$\alpha^4 + [(k_1 + 2k_2)/m + 2(k_1 \sin^2 \theta + 2k_2 \cos^2 \theta)/m_3] \alpha^2 + 2k_1 k_2 (2/m_3 + 1/m)/m = 0 \quad (24)$$

whose three roots $\alpha_1, \alpha_2, \alpha_3$, are pure imaginaries and we therefore write $\alpha_i^2 = -\mu_i^2$ from which we may obtain the normal fundamental frequencies of the system.

IV (c)

If all three particles were of the same mass, m , the foregoing expressions would simplify considerably. Under this restriction we rewrite Eq. (23):

$$\left. \begin{aligned} m\mu^2 - k_1(1 + 2 \cos^2 \theta) &= 0 \\ m^2\mu^4 - [(k_1 + 2k_2) + 2(k_1 \sin^2 \theta + 2k_2 \cos^2 \theta)]m\mu^2 + 6k_1 k_2 &= 0 \end{aligned} \right\} \quad (25)$$

The normal frequencies of this system are $\nu_i = (1/2\pi)\mu_i$ and the wave-numbers $\bar{\nu}$ are given by

$$\bar{\nu}_i = (\frac{1}{3})\nu_i \times 10^{-10} = \left(\frac{1}{6\pi} \right) \mu_i \times 10^{-10} \text{ cm}^{-1}. \quad (26)$$

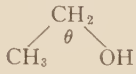
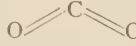
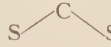
V. DETERMINATION OF THE FORCE CONSTANT k_2

Referring to section III we proceed to calculate k_2 and for that purpose we select as most suitable a molecule of ethyl alcohol, the atoms arranged in groups as shown in the accompanying table.

We assume here that the bonds form the tetrahedral (approximately 109°) angle with each other in the position of rest. As an approximation, the atomic mass of the CH_2 group is taken as fourteen while the other two groups are assigned the average mass of sixteen. The mass of each group is supposed to be concentrated at the nucleus of each heavy atom. It is to be emphasized that there is no bond acting directly between the two end groups. We may thus apply Eqs. (25) of the preceding paragraph.

We find, on using the value of k_2 found in section III: $\bar{\nu}_1 = 1035$ as compared with the observed wave-number 1047.

TABLE I.

	Structure	Force Constants	Calculated			Observed		
			1	2	3	ν_1	$\tilde{\nu}_2$	3
C_2H_5OH		$k_1=4$ $k_2=6$	1035	930	451	1047	884	450 ⁴
CO_2		$k_1=8$ $k_2=1.2$	1535	1320	703	3650	2350	683 ⁵
		$k_1=8$ $k_2=1.2$	1800	970	920			
		$k_1=32$ $k_2=4.8$	3600	1960	1820			
		$k_1=32$ $k_2=0.6$	3600	2817	978			
CS_2		$k_1=8$ $k_2=1.2$	1303	no value	no value	800	655	655 ⁴
		$k_1=4$ $k_2=6$	920	730	570			
CH_2Cl_2		$k_1=4$ $k_2=0.6$	917	1010	728	1151	715	283 ⁴
		$k_1=4$ $k_2=0.6$	1083	698	487			

⁴ A. S. Ganesan and S. Venkatesvaren, Indian Jour. Phys. **4**, 195 (1929).

⁵ R. H. Fowler, Statistical Mechanics, p. 64, Cambridge, 1929.

On using the other two fundamental wave-numbers 884 and 450 in the quadratic form (Eq. 23) we solve for k_2 , obtaining $k_2=0.6 \times 10^5$ dynes/cm as an average value. These values for the force constants had already been obtained in a very approximate manner from specific heats and Raman spectra.³

VI. SOME APPLICATIONS

We apply the results of the foregoing paragraphs to a few organic molecules, arranging the calculations in the accompanying table.

Carbon dioxide is definitely a double bonded structure and it was therefore supposed that the force constant k_1 would, in this case, be double its value for the single bond. It is found, however, that the values $k_1=32$; $k_2=0.6$ (or 1.2) dynes per cm gives results that best agree with experiment. The atomic arrangement is shown in table 2 under the heading "Structure," first with the bonds forming the tetrahedral angle and second with the atoms lying collinear. This last stable position seems to be most probable. The molecule of carbon disulphide gives best results if taken with the single bond. Dichlor methane not only seems to have a single bond structure but apparently has the straight line arrangement of its groups. Because of the agree-

³ D. H. Andrews Phys. Rev. **34**, 1626 (1929).

ment between calculated and observed data in most of the cases considered it is fairly conclusive that the force constants as determined are quite valid. The percent of error is in itself not sufficient as an objection if it is considered that the frequencies might lie in the range of 100 to 10000 wave-numbers.

The writer is greatly indebted to Professor D. H. Andrews for suggesting the problem and to Professor F. D. Murnaghan for continued advice in the preparation of the paper.

STUDY OF THE SMALL VIBRATIONS OF SIX PARTICLES
IN A SYSTEM ANALOGOUS TO THE BENZENE
RING

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(Received June 23, 1930)

ABSTRACT

The system of six particles is allowed to vibrate under certain restrictions, assuming an elastic nature for the restoring forces. Frequencies of vibration are obtained and compared with Raman data lending some support to the Claus construction of the benzene molecule.

INTRODUCTION

IN A previous paper¹ we have considered the small vibrations about a position of stable equilibrium of a system of three particles under the assumption that the forces set up by a displacement are elastic in character. It was definitely assumed that the restoring force was the sum of two types of forces; the first acting along the line of connection with another particle and proportional to the linear displacement; the second acting at right angles to the first and proportional to the change in the angle between two adjoining bonds. The results obtained for a few organic compounds pointed very strongly to the conclusion that two force constants $k_1 = 4 \times 10^5$ and $k_2 = 0.6 \times 10^5$ dynes per cm could be assigned as definite properties of the single valence bond which were independent of the particular molecule.

THEORY

In this paper we consider the system of six particles, (under the same assumptions as were taken for three particles), all of the same mass m lying in stable position at the vertices of a regular hexagon, whose side is of length a . Each particle has three connecting bonds as shown. If the angular momentum is zero and the center of gravity remains fixed, the system will have nine degrees of freedom. We, however, place certain restrictions on the motion of the system that will reduce considerably the order of the resulting characteristic determinant. The motion of the particles is assumed to be in a given plane and higher order infinitesimals, in the presence of those of lower order, are neglected throughout.

First we allow only motion along the 60 degree lines passing through the center of the hexagon. Let: (a) the displacement of the i^{th} particle from its position of rest be x_i ; (b) the change in the corresponding angles formed by the bonds be θ_i , and ϕ_i ; (c) the change in the length of the outside bonds be Δ_i . We have:

¹ R. C. Yates, The Elastic Character of the Homopolar Chemical Bond, p. 555, this issue.

$$\Delta_i = (x_i + x_{i+1})/2 \quad (i = 1, \dots, 6)$$

The energy functions are set up at once, following the procedure of the first paper:

$$\left. \begin{aligned} T &= (m/2) \cdot \sum_1^6 \dot{x}_i^2 \\ V &= (k_1/2) \cdot \sum_1^6 (\Delta_i^2 + x_i^2/2) + (a^2 k_2/2) \cdot \sum_1^6 (\theta_i^2 + 2\phi_i^2) \end{aligned} \right\} \quad (1)$$

If the center of mass is to remain fixed: $x_1 = x_4$, $x_2 = x_5$, $x_3 = x_6$, leaving three independent coordinates to fix the system.

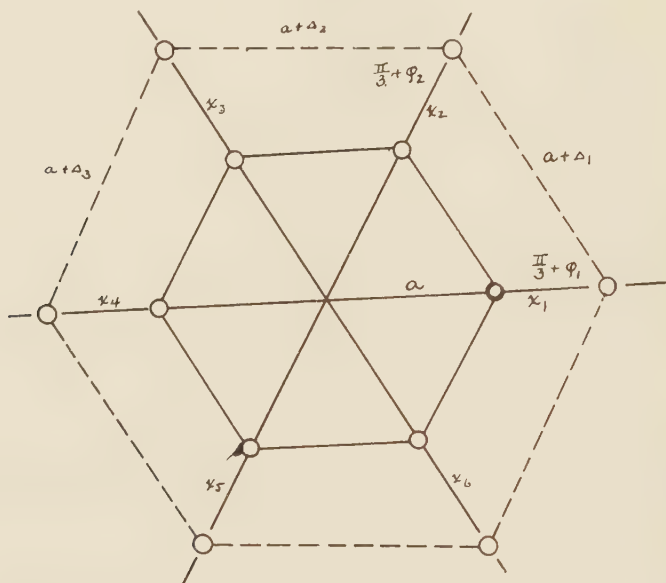


Fig. 1. Vibration along radial lines.

From the figure $\phi_1 = (3^{1/2}/a)x_2$, $\phi_2 = (3^{1/2}/a)x_3$, etc. and since $\theta_1 = \phi_1 - \phi_6$ etc., we may write Eqs. (1) in the final form:

$$\left. \begin{aligned} T &= m \cdot \sum_1^3 \dot{x}_i^2 \\ V &= (k_1/2) (2 \sum_1^3 x_i^2 + x_1 x_2 + x_1 x_3 + x_2 x_3) \\ &\quad + 6k_2 \left(2 \sum_1^3 x_i^2 - x_1 x_2 - x_1 x_3 - x_2 x_3 \right) \end{aligned} \right\} \quad (2)$$

The equations of motion are accordingly:

$$\left. \begin{aligned} 2m\ddot{x}_1 &= -(k_1/2)(4x_1 + x_2 + x_3) - 6k_2(4x_1 - x_2 - x_3) \\ 2m\ddot{x}_2 &= -(k_1/2)(x_1 + 4x_2 + x_3) - 6k_2(-x_1 + 4x_2 - x_3) \\ 2m\ddot{x}_3 &= -(k_1/2)(x_1 + x_2 + 4x_3) - 6k_2(-x_1 - x_2 + 4x_3) \end{aligned} \right\} \quad (3)$$

On combining the Eqs. (3), we find the set of normal coordinates

$$z_1 = x_1 + x_2 + x_3 \quad z_2 = x_1 - x_2 \quad z_3 = x_2 - x_3$$

with resulting frequencies:

$$\left. \begin{aligned} \nu_1 &= \left(\frac{1}{2\pi}\right) [(3k_1 + 12k_2)/m]^{1/2} \\ \nu_2 = \nu_3 &= \left(\frac{1}{4\pi}\right) [(3k_1 + 60k_2)/m]^{1/2} \end{aligned} \right\} \quad (4)$$

Secondly, we restrict the system to motion on a circle of arbitrary radius $(a+b)$. We select a polar system of reference with pole at the mass center and initial line passing through a vertex of the hexagon.

Let: (a) the angular displacement of the particles be θ_i ; (b) the change in the angles between adjoining bonds be $\alpha_i, \beta_i, \phi_i$, where $\phi_i = \alpha_i + \beta_i$; (c) the change in the bond length be Δ_i .

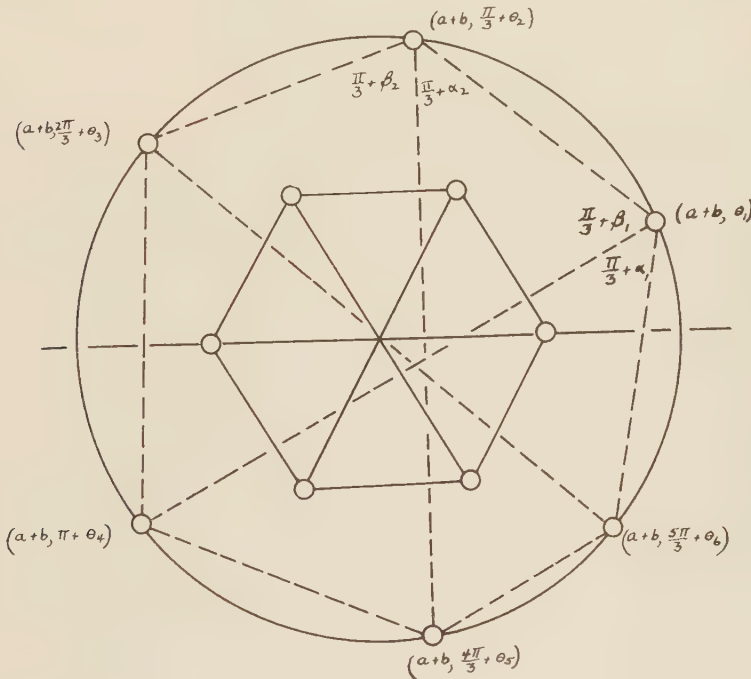


Fig. 2. Vibration on a circle.

The energy functions are:

$$\left. \begin{aligned} T &= (m/2)(a+b)^2 \sum_1^6 \dot{\theta}_i^2 \\ V &= (k_1/2) \left[\sum_1^6 \Delta_i^2 + 3b^2 \right] + (a^2 k_2/2) \sum_1^6 (\alpha_i^2 + \beta_i^2 + \phi_i^2) \end{aligned} \right\} \quad (5)$$

From an inspection of the figure we find

$$\left. \begin{aligned} \alpha_1 &= (2\theta_6 - \theta_1 - \theta_4)/2 & \beta_1 &= -(2\theta_2 - \theta_1 - \theta_4)/2 \\ \alpha_2 &= (2\theta_1 - \theta_2 - \theta_5)/2 & \beta_2 &= -(2\theta_3 - \theta_2 - \theta_5)/2 \end{aligned} \right\} \quad (6)$$

etc. which give expressions for ϕ :

$$\phi_i = \phi_{i-1} - \phi_{i+1}. \quad (7)$$

In order to fix the center of gravity at the pole we must have

$$\left. \begin{aligned} \theta_5 &= \theta_1 + \theta_2 - \theta_4 \\ \theta_6 &= -\theta_1 + \theta_3 + \theta_4 \end{aligned} \right\} \quad (8)$$

If we now put angular momentum about the center of mass equal to zero we obtain the further relation $\sum_1^n \dot{\theta}_i = 0$. We thus eliminate θ_4 , θ_5 , and θ_6 by means of the equations:

$$\left. \begin{aligned} \theta_4 &= -\theta_1 - 2\theta_2 - 2\theta_3 \\ \theta_5 &= 2\theta_1 + 3\theta_2 + 2\theta_3 \\ \theta_6 &= -2\theta_1 - 2\theta_2 - \theta_3 \end{aligned} \right\} \quad (9)$$

We obtain now also from the figure

$$\left. \begin{aligned} \Delta_1 &= b + [a(3)^{1/2}/2](\theta_2 - \theta_1) & \Delta_4 &= b + [a(3)^{1/2}/2](3\theta_1 + 5\theta_2 + 4\theta_3) \\ \Delta_2 &= b + [a(3)^{1/2}/2](\theta_3 - \theta_2) & \Delta_5 &= b - [a(3)^{1/2}/2](4\theta_1 + 5\theta_2 + 3\theta_3) \\ \Delta_3 &= b - [a(3)^{1/2}/2](\theta_1 + 2\theta_2 + 3\theta_3) & \Delta_6 &= b + [a(3)^{1/2}/2](3\theta_1 + 2\theta_2 + \theta_3) \end{aligned} \right\} \quad (10)$$

With the foregoing expressions we may rewrite Eqs.(5) explicitly in terms of the three remaining independent coordinates θ :

$$\left. \begin{aligned} T &= m(a+b)^2[5\dot{\theta}_1^2 + 9\dot{\theta}_2^2 + 5\dot{\theta}_3^2 + 12\dot{\theta}_1\dot{\theta}_2 + 8\dot{\theta}_1\dot{\theta}_3 + 12\dot{\theta}_2\dot{\theta}_3] \\ V &= (k_1/2)[9b^2 + (3a^2/2)(36\theta_1^2 + 60\theta_2^2 + 36\theta_3^2 + 84\theta_1\theta_2 + 60\theta_1\theta_3 + 84\theta_2\theta_3)] \\ &\quad + a^2k_2[24\theta_1^2 + 60\theta_2^2 + 24\theta_3^2 + 66\theta_1\theta_2 + 30\theta_1\theta_3 + 66\theta_2\theta_3] \end{aligned} \right\} \quad (11)$$

The corresponding equations of motion are:

$$\left. \begin{aligned} m(a+b)^2(5\ddot{\theta}_1 + 6\ddot{\theta}_2 + 4\ddot{\theta}_3) &= -\left(\frac{9a^2k_1}{2}(6\theta_1 + 7\theta_2 + 6\theta_3) \right. \\ &\quad \left. - 3a^2k_2(8\theta_1 + 11\theta_2 + 5\theta_3) \right) \\ m(a+b)^2(2\ddot{\theta}_1 + 3\ddot{\theta}_2 + 2\ddot{\theta}_3) &= -\left(\frac{3a^2k_1}{2}(7\theta_1 + 10\theta_2 + 7\theta_3) \right. \\ &\quad \left. - a^2k_2(11\theta_1 + 20\theta_2 + 11\theta_3) \right) \\ m(a+b)^2(4\ddot{\theta}_1 + 6\ddot{\theta}_2 + 5\ddot{\theta}_3) &= -\left(\frac{9a^2k_1}{2}(5\theta_1 + 7\theta_2 + 6\theta_3) \right. \\ &\quad \left. - 3a^2k_2(5\theta_1 + 11\theta_2 + 8\theta_3) \right) \end{aligned} \right\} \quad (12)$$

If here we make the change of variables: $z_1 = 2\theta_1 + 3\theta_2 + \theta_3$, $z_2 = \theta_1 + 3\theta_2 + 2\theta_3$, $z_3 = \theta_1 - \theta_3$, the last set of equations may be replaced by:

$$m(a+b)^2\ddot{z}_i = -9a^2(k_1/2 + k_2)z_i \quad (i = 1, 2, 3). \quad (13)$$

The characteristic of the differential Eqs. (12) is degenerate and for this particular type of motion there is but one frequency:

$$\nu = [3a/2\pi(a+b)][(k_1 + 2k_2)/2m]^{1/2}.$$

CONCLUSION

If the hydrogens in the benzene ring are grouped with the carbons and if we assume bonds passing through the center of the hexagon we may apply our results. Using the values for the elastic constants which were secured in the previous paper² the values for the three characteristic frequencies are found, as shown in Table I.

TABLE I.

Force constants	ν Calculated	ν Observed ⁴
$k_1 = 4 \times 10^5$	—	605
	—	849
$k_2 = 0.6 \times 10^5$	—	991
	1145	1176
	1305	
	1750	—

The frequencies in the Raman spectra, believed to be associated with the carbon atoms, are also given. Now it has already been deduced from a study of the relation between Raman spectra³ that the experimentally observed frequency of 1176 cm^{-1} should correspond to the type of motion where all the carbon atoms move in and out together along the lines through the center of the hexagon. The agreement between this value and the calculated one of 1145 cm^{-1} substantiates this view and indicates that the values chosen for the elastic constants are fairly correct. The other two calculated frequencies fail to agree with any of those experimentally observed. It appears probable that for these the restrictions imposed on the motion were so far removed from the actual state of the molecule that these types of motion do not exist in actuality.

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² R. C. Yates, reference 1.

³ C. F. Kettering, L. W. Shutts, and D. H. Andrews, *Phys. Rev.* **36**, 531 (1930). D. H. Andrews, *Phys. Rev.* **36**, 544 (1930).

⁴ A. S. Ganesan and S. Venkateswaran, *Indian Jour. Phys.* **4**, 195 (1929).

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